# MISSOURI DEPARTMENT OF NATURAL RESOURCES
# DIVISION OF ENVIRONMENTAL QUALITY
# ENVIRONMENTAL SERVICES PROGRAM
# Standard Operating Procedure

SOP #: MDNR-FSS-100 EFFECTIVE DATE: July 18, 2001

TITLE: Field Analysis of Water Samples for pH

WRITTEN BY: Trish Rielly, Environmental Specialist, Water Quality Monitoring Section, ESP

APPROVED BY: Douglas N. Edwards, Acting Director, ESP

SUMMARY OF REVISIONS: Major revisions have been made to the sampling plan and procedures to reflect the newer pH meter models used.

APPLICABILITY: The procedures outlined in this sampling protocol apply to ESP personnel who analyze for pH in the field.

DISTRIBUTION: MoDNR Intranet
ESP FSS Supervisor
FSS SOP Coordinator

RECERTIFICATION RECORD:

| | | | | |
|---|---|---|---|---|
| Date Reviewed | | | | |
| Initials | | | | |

## 1.0 SCOPE AND APPLICABILITY

1.1 This Standard Operating Procedure provides the Environmental Services Program (ESP) field personnel with guidance on the operation and maintenance of the various pH meters and how to conduct analysis of pH during their field investigations.

1.2 Measurement of pH is one of the most frequently used tests in water chemistry. It is an indication of the acidic or basic character of a solution and is based on the activity of the hydrogen ion measured on a scale of 0 to 14. The measurement of pH is expressed as the logarithm of the reciprocal of the hydrogen ion concentration. Hence "p" the mathematical symbol of the negative logarithm, and "H", the chemical symbol of hydrogen (refer to Omega 1990/1991, The pH and Conductivity Handbook).

1.3 A change in one pH unit represents a ten-fold change in the effective strength of an acid or base. All pH measurements are temperature dependent, which means they will vary according to the temperature of the solution. For example, at 25°C, a pH of 7.0 is considered neutral where the activities of the hydrogen and the hydroxyl ions are equal. However, at 0°C a pH of 7.5 is considered the neutral point.

1.4 A pH of 6.5 - 9.0 is the acceptable pH range for most aquatic life. The pH of Missouri rivers and streams are generally between 6.5 - 8.5 pH units. Refer to Table 1 for pH of Common Substances and pH Limits for Aquatic Life.

## 2.0 PERSONNEL QUALIFICATIONS

Field personnel shall have a working knowledge of the field sample collection procedures and will have at a minimum either attended the department-sponsored inspection and enforcement training or received training from an MDNR employee knowledgeable of the proper sample collection procedures.

## 3.0 HEALTH AND SAFETY

Most field activities involving the collection of pH measurements will likely include working in and/or around a type of waste stream or waste storage system. Field personnel are encouraged to protect themselves by wearing the appropriate level of personnel protection equipment.

## 4.0 SAMPLING CONSIDERATIONS

4.1 Temperature can have two effects on the electrometric (pH meters/pens using glass or combination electrodes) measurement of pH. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode/instrument system at the sample's temperature. The second cause is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled; therefore, it should be noted by reporting both the pH and sample temperature at the time of analysis (*Methods* *for Chemical Analysis of Water and Wastes, 1983, EPA Method 150.1 (Electrometric)*).

4.2 A pH sample has no holding time and should be analyzed immediately upon collection. Except in rare instances, pH analysis should be performed on grab samples only.

4.3 The pH is recorded in terms of a pH unit and should be reported to the nearest 0.1 unit.

4.4 The glass electrodes have a porous ceramic junction that electrolyte solution must flow through in order to obtain a pH reading. This junction can become blocked by petroleum products, metals, proteins, etc. Common situations where electrode malfunctions may occur are at landfills, mining areas, wastewater influent, and in determining the characteristics of unknowns. When analyzing these sample types, choose the type of equipment that is least expensive to replace but still meets the sampling requirements. Electrode cleaning and reconditioning procedures can be found in Appendix A.

## 5.0 GENERAL OVERVIEW

5.1 The ESP uses various types of equipment to measure pH: Orion Model 230A and Orion Model 230A+ pH meters, pH pens and pH paper. The meters and pens are capable of one- or two-point calibration and will automatically compensate for temperature differences between tested solutions.

5.2 All pH meters and pens must be calibrated at two points that bracket the expected pH of the sample (*Methods for Chemical Analysis of Water and Wastes, 1983, EPA Method 150.1 (Electrometric)*). Therefore, measurements made with one-point calibrated instruments or pH paper may not be acceptable for all applications (e.g. enforcement actions).

5.3 pH paper should only be used as a screening tool or when accuracy is not important.

5.4 The meters and pens should be calibrated at least once per day just prior to the collection of field measurements. If numerous samples are to be collected, the pH meter should be checked in buffer solution to ensure the meter is holding calibration throughout the day. When the meter is not capable of reading within ± 0.5 pH units of the buffered solution the meter should be recalibrated. The meters and pens shall be calibrated according to the manufacturer’s instructions using known buffered standards that bracket the anticipated pH of the sample (e.g., 7.0 - 4.0 or 7.0 - 10.0).

5.5 Calibration procedures should be documented in a field notebook (refer to MDNR-FSS-004 *Field Documentation*).

## 6.0 GENERAL pH MEASUREMENT PROCEDURES FOR ALL pH METERS USED BY ESP

6.1 Immerse the pH electrodes in an adequate amount of sample solution to completely submerge the electrode junction and gently stir until a stable reading is achieved.

6.2 Record the pH measurement on the Chain-of-Custody Record form (refer to MDNR-FSS-002

*Field Sheet and Chain-of-Custody Record*) and/or in the field personnel's field notebook.

6.3 To prevent cross contaminating a sample, the pH electrode should be rinsed with deionized water after use and between measurements and blotted dry with a soft cloth or paper towel.

## 7.0 pH DETERMINATION USING THE ORION MODEL 230A AND MODEL 230A+ pH METERS

7.1 Both meters are characterized by a digital display, a key pad and one of two types of pH electrodes:

Glass rugged pH electrode with a separate automatic temperature compensation (ATC) electrode may be used with the Orion Model 230A and 230A+ pH meters. The advantage of using this type of electrode is that it has a high degree of accuracy and a fast response time. The disadvantage is that if damaged, this type of probe is expensive to replace. Glass electrodes are relatively rugged however they will break if mistreated.

Gel-filled epoxy-bodied electrode may also be used with the Orion meters. This type of electrode combines the pH, reference, and ATC electrodes, and is referred to as triode electrode. The triode electrode is more durable for field use, however, it is not easy to troubleshoot and, therefore, tends to have a shorter life span. Since pH is temperature dependent, the gel has to warm or cool to the solution's temperature before a stable reading can be obtained. As a result the triode has a slower response time.

7.2 Calibration Procedures for the Orion Model 230A and Model 230A+ pH meters

The power up procedure should be followed prior to field use to ensure that the meter's electronic and hardware components are in working order. The self-test checkout procedure should be conducted whenever troubleshooting becomes necessary.

7.2.1 Power up procedure:

a. Attach the BNC shorting plug to the BNC connector on top of meter.
b. Press power key to turn meter on.
c. If battery indicator remains on, replace the battery.
d. Press the power key to turn meter off.

7.2.2 Self-test checkout procedure:

a. Press and hold the YES key while pressing the POWER key.
The instrument automatically performs electronic and hardware diagnostic tests.
b. After code 7 a "0" will appear on the display. Press each key (the numeric digits displayed will change with each key press). All keys must be pressed within 10 seconds to complete "test 7".
c. After the keypad test (test 7) the meter will automatically turn off.
d. If any problems are found during the self-test, the meter will display the operator assistance code until the YES key is pressed. Refer to the operation manual for a list of the operator assistance codes.

e. If the operator does not wish to perform the self-diagnostics checkout, the meter may be turned on by pressing the POWER key.

7.2.3 This model of pH meter has two means of calibration. The meter may be calibrated by performing either the autocalibration method or manual calibration method. Both methods are capable of either one- or two-point buffer calibration.

- <u>Autocalibration method</u>: The meter automatically recognizes the buffers 4.01, 7.00 and 10.01 within the range of ± 0.5 pH units (recognition greater than ± 0.5 pH units will trigger an operator assistance code). Once the electrode is stable, the meter automatically recognizes and displays the temperature-corrected value for that buffer. If the ATC probe is not used, all samples and buffers should be at the same temperature or manual temperature compensation should be used. Refer to the Orion Model 230A or Model 230A+ operational manual for further assistance.

- <u>Manual calibration method</u>: To calibrate with buffers other than 4.01, 7.00 or 10.01, the calibration sequence is the same as autocalibration except that the buffer values are scrolled in. Again, if the ATC probe is not used all samples and buffers should be at the same temperature or manual temperature compensation should be used. Refer to the Orion Model 230A or Model 230A+ operational manual for further assistance.

7.3 A summary version of the autocalibration method is included in each pH meter case. For a description of the aforementioned calibration methods, please refer to the Orion Model 230A or Model 230A+ operational manual.

7.3.1 Meter Setup for Calibration:

a. Press the POWER key to turn meter on. The main display should read a steady 7.00 ± 0.02.
b. If not, press the CAL key, when the display flashes 7.00 press yes.
c. If not, scroll until the display reads 7.00 then press YES.
d. Press MEASURE. The main display should read 100.0 with the legend SLP in the lower display. If so, press YES.
e. If not, scroll until the display reads 100.0 then press YES. The meter advances to measure and the display should now read a steady 7.00.

7.3.2 For two-point calibration, use the following calibration instructions.

a. Remove the BNC shorting plug and connect the electrodes to the meter. Choose either 4.01 and 7.00 or 7.00 and 10.01 buffers, whichever will bracket the expected sample range.
b. Place electrode(s) into 7.00 buffer.
c. Press CAL. Calibration is displayed above the main readout and P1 is displayed in the lower field. P1 indicates that the meter is ready for the first buffer. When the electrode is stable the READY prompt will be displayed and the temperature-corrected value for the buffer is displayed. If the desired buffer is recognized

press YES to accept. If the buffer is not recognized, press a scroll key, ▲ or ▼, to change the buffer reading. The display will remain frozen for two seconds then P2 will be displayed in the lower field indicating the meter is ready for the second buffer.

d. Rinse the electrode(s) with D.I. water and pat dry. Place the electrode(s) in the second buffer (4.01 or 10.01) and wait for a stable pH display. If the desired buffer is recognized press YES. If the buffer is not recognized, press a scroll key, ▲ or ▼, to change the buffer reading and press YES. After the second buffer value has been entered, the electrode slope will be displayed. SLP appears in the lower field while the actual electrode slope (in percent) appears in the main field.
e. The meter automatically advances to the measure mode. MEASURE is displayed above the main field.
f. Rinse electrode(s) and pat dry, then place into sample. Record pH and temperature directly from the meter display.

7.3.3 Determination of pH for water samples.

a. Rinse electrode(s) with D.I. water and pat dry.
b. Place electrode(s) in a volume of sample that covers the electrode junction.
c. Stir gently and wait for a stable reading.
d. When measuring the pH of low ionic strength samples, it is advisable to repeat the "stir and stabilize" cycle several time until the reading no longer fluctuates.
e. Record the pH result to the nearest 0.1 pH unit on the Chain-of-Custody Record form and/or in a field notebook.
f. After use, rinse the electrode(s) with D.I. water to minimize contamination.

## 8.0 pH DETERMINATION USING A pH PEN

8.1 At a minimum, a two-point calibrated pH pen should be used (refer to *Standard Methods for the Examination of Water and Wastewater, 1995, 19th Edition, section 4500-H$^+$).* The pH pen is simple to use and is fairly accurate and reliable. Appropriate uses for the pH pen are similar to those for pH paper. It is a good back-up system in case of meter malfunction. The pen is a low cost piece of equipment and, therefore, more appropriate to use on caustic solutions or solutions containing petroleum products. Another appropriate application is to determine the hazardous characteristics of an unknown. However, the pen should not be used if a high degree of accuracy is required.

8.1.1 Two-point calibration procedures

a. Choose two buffer solutions that will bracket the desired pH range.
b. Remove the cap and turn on the pen by pressing the button located on the top of the pen.
c. Rinse the bottom of the pH electrode (the indented portion that indicates how far the pen should be immersed in solution) with D.I. water.
d. Shake off excess water and blot dry with a paper towel.

e. Immerse the pen into the 7.00 buffer solution up to the immersion level.
f. Stir gently and wait for the display to stabilize.
g. Using a small screwdriver, turn the "pH 7" calibration trimmer (small recessed screw) located on the back of the pen until the displayed value matches the 7.0 buffer value.
h. Rinse the bottom of the pH electrode with D.I. water, shake off excess water and blot dry with a paper towel.
i. Immerse the pen into the second buffer solution (pH 4.01 or pH 10.01).
j. Stir gently and wait for the display to stabilize.
k. Again, using the small screwdriver, turn the "pH 4/pH 10" calibration trimmer until the displayed value matches the buffer value.
l. Two-point calibration is now complete.

8.1.2 Determination of pH for water samples

a. Rinse the electrode with D.I. water.
b. Shake off excess water and pat dry with paper towel.
c. Immerse pen into the sample up to the immersion level.
d. Stir gently and wait for the display to stabilize.
e. Record the result to the nearest 0.1 pH unit on the Chain-of-Custody form.
f. After use, rinse the electrode with D.I. water to minimize contamination.

## 9.0 pH DETERMINATION USING pH PAPER

9.1 pH paper is the simplest, least expensive and least accurate method for determining pH. There are situations where the use of pH paper is appropriate. It can be used as a quick and easy screening tool. In case of a meter malfunction, it can be a viable back-up system. It can easily be used on very acidic or alkaline solutions where the color change is dramatic. It may also be the method of choice when analyzing the pH of sludges or very viscous solutions. The greatest disadvantage of using pH paper is that the readings are subjective and dependent upon the visual judgement of the analyst. In addition, any color associated with the liquid being analyzed may interfere with the reading.

9.2 To determine the pH of a water sample, immerse a portion of the paper into the liquid to be analyzed. Compare the resulting color change to the color chart supplied by the manufacturer.

## 10.0 QUALITY CONTROL

10.1 The pH meters and pens should be calibrated at least once a day just prior to the collection of field measurements. If numerous sites are to be monitored, the meters/pens should be periodically rechecked in pH buffer solution throughout the day. When the meter is not capable of reading within ± 0.5 pH units of the buffered solution the meter should be recalibrated.

10.2 The ESP pH meters and pens are subjected to monthly QC checks. The meters are calibrated and checked for accuracy by WQMS personnel using a known certified standard solution.

10.3 As part of quality control, all meters must be checked out by field personnel prior to field use. The following information shall be recorded on the equipment sign-out sheet: meter type(s) and property number(s), date meter(s) were checked out and returned, and the user's name. Upon return from the field, field personnel shall record any problems/comments when using the meter in the comment section of the sign-out sheet.

## 11.0 REFERENCES

Hanna Instruments pHep 2 Pocket-Sized pH Meter Instruction Manual.

MDNR-FSS-001 *Required/Recommended Containers, Volumes, Preservatives, Holding Times and Special Considerations.*

MDNR-FSS-002 *Field Sheet and Chain-of-Custody Record*.

MDNR-FSS-005 *General Sampling Considerations Including the Collection of Grab, Composite, and Modified Composite Samples for Streams and Wastewater Flows*.

Omega 1990/1991, The pH and Conductivity Handbook.

Orion Laboratory Products Group Portable pH/ISE Meters Instruction Manual for Model 230A, Model 250A, Model 290A.

Standard Methods for the Examination of Water and Wastewater, 1995, 19th Edition.

The Adopt-A-Stream Foundation Streamkeeper's Field Guide, 1999.

## Table 1

## pH of Common Substances and pH Limits for Aquatic Life

| | | | |
|---|---|---|---|
| **0** | *(Acidic)* **Battery Acid** | | |
| **1** | **Lemon Juice** | | |
| **2** | **Coca cola** **Vinegar** | **All fish dead** | **Sediments release metals into water in forms toxic to aquatic life** |
| **3** | | | |
| **4** | **Orange juice** | | |
| **5** | **Rain** | **Fish and tadpoles begin to die** | |
| **6** | | | |
| **7** | **Distilled water** | **Optimal range for most aquatic life (6.5 - 8.2)** | |
| **8** | **Baking soda** | | |
| **9** | | | |
| **10** | | **Fish and tadpoles begin to die** | |
| **11** | **Ammonia** | | |
| **12** | **Bleach** | **All fish dead** | |
| **13** | **Lye** | | |
| **14** | *(Basic)* | | |

*1999, The Adopt-A-Stream Foundation Streamkeeper's Field Guide*

**Appendix A**
**MDNR-FSS-100**

## Maintenance and Storage Procedures for pH Meters, Pens and Electrodes

In general, the pH electrodes should be stored according to the manufacturer's recommendations.

- Orion Gel-filled epoxy electrodes: store the electrode in the plastic protective cap with a few drops of electrode storage solution.
- Glass Orion electrodes: store the pH electrode in the plastic protective cap with a few drops of electrode storage solution. The ATC electrode is stored dry and within the plastic protective cap.
- pH pens: store the electrode with a few drops of electrode storage solution or pH 7.0 solution in the protective cap.

## Electrode Cleaning Procedures for the Orion Glass Electrode

As a general cleaning procedure, soak pH electrode in 0.1M HCl solution for approximately one hour. Then soak in appropriate storage solution for one hour.

For complete reconditioning procedures follow the following steps:

- Soak in 0.1M HCl to remove protein deposits.
- Soak in 0.1M EDTA for 15 minutes to remove inorganic deposits.
- Wash with soap and water and/or soak in methanol for approximately 15 minutes (acetone may be substituted) to remove oil and grease deposits.
- Soak in 0.1M KOH for 15 seconds. Then soak in 0.1M HCl for 15 seconds. Repeat cycle several times. This conditions the membrane glass.
- Soak in appropriate storage solution for one hour. If possible, it is recommended that the electrode chamber be emptied and refilled after reconditioning.

Note: Rinse all electrodes with D.I. water after immersing in any solution.